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The phosphorous pentoxide electrolytic hygrometer

by

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(Clarendon Laboratory Oxford)

AIR MINISTRY

METEOROLOGICAL RESEARCH COMMITTEE

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Since about June, 1956, descriptions of a new hygrometer originating in the Dupont Laboratories, have appeared in the U.S. technical literature (1),(2). and several U.S. instrument firms are now offering hygrometers based on the new principle. All the literature refers to its use at concentrations of a few parts per million (p.p.m.). Since a F.P. (frost point) of -80°C equals 0.4 p.p.m. it is possible that the hygrometer could be used in arctic conditions and in upper atmosphere measurements. This note briefly reviews this possibility.

Principle of operation

The detector consists in principle of a film of phosphoric acid covering a fine grid of platinum electrodes. The electrodes are formed from two fine platinum wires (.004 in. diameter) wound as a two start thread and with a spacing of about .004 in. between adjacent electrodes. A potential difference, which must be greater than 2v and is usually about 50v, is applied between the wires. This electrolyses the water in the phosphoric acid to hydrogen and oxygen, and the phosphoric acid is converted to partially hydrolysed P_2O_5. As this happens the resistance rises and eventually the current is cut off. If now a measured volume of air is passed over the element the P_2O_5 will absorb the water contained in the air and conduct electricity until the water has been electrolysed away. The quantity of electricity passed is determined by the quantity of water absorbed and Faraday's laws of electrolysis, and <u>not</u> by the resistance of the film.

The instrument works as a continuous detector when there is a controlled flow of air, and subject to lag, the current passing depends only on the water content of the air stream.

The absorption of all the water from the air presents difficulties if the air flow exceeds about 200 cc/min, but this is quite convenient as the following approximate calibration shows:

/1 gm H_2O

$$1 \text{ gm } H_2O = 10.6 \times 10^3 \text{ coulombs}$$

F.P.	Water vapour density gm/cc	Current at 3 cc of air/sec
-80°C	4.5×10^{-10}	14.0 μa
-60°C	8×10^{-9}	250.0 μa
-40°C	1×10^{-7}	3.2 ma
-20°C	8×10^{-7}	25.0 ma
0°C	4.7×10^{-6}	150.0 ma
+20°C	1.7×10^{-5}	540 ma

It will be seen that the currents are quite easily measurable but the range is uncomfortably large. At the large water contents resistive heating is said to be a nuisance. Published accounts claim that the instrument is usable over at least the range of F.P. -80°C to -20°C.

Response time Published data give exponential response times of one minute for increasing water contents and two minutes for decreasing water contents.

Specificity There is no reason to expect any other atmospheric constituent to interfere with its operation.

Construction of the element

The element, as described, is made by winding the platinum wires with copper wires as spacers on a 1 mm to 0.75 mm diameter mandrel for a length of approximately 30 cm; embedding this in Polytetrafluorethylene, removing the mandrel and then dissolving the copper away with acid. In this way the wires are obtained on the outside of a 1 mm (approx) diameter capillary tube 30 cm long. For convenience a coiled coil arrangement is adopted making the final element of reasonable dimensions.

Reliability

Published accounts claim good reliability. One instrument passed to the writer for test failed immediately tests began and this is similar to the experience of the only other person I have met who has actually used one.

Special considerations for meteorological use

Back pressure

The back pressure due to the "Poiseuille" drag in the tube of an element of this construction would be of the order of 20-50 mb depending very much on the actual diameter of the hole and the roughness of the walls, but not on the total pressure. For meteorological purposes this is too large, since, in order to avoid contamination of the air it must be drawn through the element, and this back pressure becomes too large a fraction of the total air pressure.

There is no reason in principle why this should not be overcome by using an annular gap of about 0.5 mm between a cylinder, say 5 mm diameter, and a tube 6mm diameter, but there may be practical difficulties. For this, 2 cm length is sufficient for approximately 99 per cent extraction, with negligible back pressure. The extraction efficiency will improve at high levels due to the increasing diffusion coefficient at low pressures.

Flow measurement

At flow rates of about 200 cc/minute our experience is that the most satisfactory method of flow control is to use a small positive displacement piston pump, either driven by a constant speed motor, or with a variable speed motor, and measure the rate of rotation of the motor. For the latter we have used a 40 mm^3 pump running at approximately 5000 r.p.m. and we are making a prototype pump for use with a constant speed motor.

Effect of lag and the wide range of water contents in the atmosphere

A special circumstance arises from the wide range of water contents encountered in the atmosphere. During an ascent when climbing at a rate of say 1500 ft per minute the average rate of fall of water content is greater than through a ratio 1:1/e in two minutes, which is the maximum rate of response claimed for falling water contents. This rate of response is therefore inadequate for use on balloons and would not permit use in aircraft during rapid ascents or descents. For this an exponential response time of about 30 sec. is desirable.

Conclusion

Though it is by no means free from difficulties it would seem that this is a very hopeful hygrometer which would certainly be suitable for arctic conditions and for some kinds of upper air work.

Mr. Goldsmith at A.E.R.E., is working on a practical development for high altitude work.

Acknowledgment

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References

(1) F. A. Keidel "A novel and inexpensive instrument for accurate analysis for traces of water". Du Pont de Nemours & Co., Inc., Wilmington, Delaware. Presented February 27th, 1956 Pittsburgh conference on Analytical Chemistry and Applied Spectroscopy.

(2) E.S. Taylor "New instrument for the moisture analysis of 'Freon'" Refrigerating Engineering, July, 1956, p.41.